Abstract Submitted
for the SHOCK13 Meeting of
The American Physical Society

Identification of TS structures by a combination of high pressure kinetics and MD volume calculations HEATHER WIEBE, JACOB SPOONER, Simon Fraser University, NOHAM WEINBERG, University of the Fraser Valley, Simon Fraser University — In order to use transition state theory (TST) to describe the kinetics of conformational changes in large macromolecules, such as proteins, the transition state (TS) for the process must be well defined. However, the extremely long timescales and high dimensionality of such processes make identification of the TS difficult using traditional molecular dynamics (MD) techniques. We propose to identify TS structures using their volumetric properties. The effect of pressure on reaction rates is traditionally expressed in terms of logarithmic pressure derivatives, known as activation volumes. According to TST, activation volumes can be identified as the difference in volume between the TS and reactant species: $-RT(\partial \ln k/\partial P)_T = \Delta V^{\neq} = V^{\neq} - V_R$. Recently, a method was developed[1] which uses MD simulations for calculation of accurate theoretical volumes of activation. MD volumes can also be calculated for any transient structure along reaction coordinate, y, to produce theoretical volume profiles $\Delta V_{MD}(y)$. If the position $y^{\neq}$ of the TS along the reaction coordinate is unknown, it can be found by locating $\Delta V^{\neq}$ on the MD-generated volume profile: $\Delta V_{MD}(y^{\neq}) = \Delta V^{\neq}$. In this work we present a successful test of our methodology for two model systems: isomerization in a bistable diatomic and conformational changes in a long chain with strongly interacting termini.

[1]H. Wiebe et al, J. Phys. Chem. C, 2012, 116, 2240–2245; J. Spooner et al, Phys. Chem. Chem. Phys., 2012, 14, 2264-2277.

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Date submitted: 22 Feb 2013 Electronic form version 1.4